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THE ETCH MECHANISM FOR Al_2O_3 IN FLUORINE AND CHLORINE BASED RF DRY ETCH PLASMAS

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ABSTRACT

The etch behaviour of Al_2O_3 was studied in Ar, CHF_3/Ar, CF_4/O_2 and Cl_2 low pressure RIE plasmas. The influence of dc self-bias voltage, wafer temperature, gas flow and pressure on the Al_2O_3 etch behaviour was investigated. This was compared with the etch behaviour of SiO_2, Mo, Au and Si under the same conditions. It was found that even though aluminum does not form volatile fluorides addition of CHF_3 to an Ar plasma resulted in a ninefold increase in the Al_2O_3 etch rate. This compares to a fivefold increase in the SiO_2 etch rate and a 20% decrease in Au etch rate.

An Al_2O_3 etch mechanism for fluorine based plasmas is proposed, comprising of the formation of AlF_x and its subsequent removal under influence of high energy ion bombardment. The latter appears to be the rate limiting step.

INTRODUCTION

Plasma-assisted etching involves the interaction of a glow discharge with a solid surface to produce a volatile product. From this perspective it is not surprising that the patterning of Al_2O_3 layers is considered to be a non-trivial matter in plasma etching, using either fluorine based or chlorine based plasmas. Aluminum fluorides are not volatile at room temperature and the breakdown of Al_2O_3 to form a volatile chloride requires a relatively high energy ion bombardment [1].

For certain applications (e.g. thin film magnetic heads) Al_2O_3 is an attractive alternative to SiO_2 as a dielectric. However, the implementation of Al_2O_3 requires a reliable dry etch process.

This work describes reactive ion etching of Al_2O_3 in fluorine and chlorine based rf dry etch plasmas. The Al_2O_3 etch rate is discussed as a function of gas composition, flow, and pressure, temperature and dc self-bias voltage. To investigate the etch mechanism of Al_2O_3 its etch behaviour is compared with the etch behaviour of SiO_2, Si, Mo and Au under the same conditions. In an attempt to separate the physical and chemical mechanisms their etch behaviour was also studied in an Ar plasma.

THEORY

Lee et al. [2] suggested that the etch rate during reactive ion etching (ER) should be written as:

$$ER = K_i V_{dc}^{2.5} + K_c N \qquad \text{equation (1)}$$

where K_i is the constant for the ion bombardment induced etching, K_c is the constant for the chemical etching (this is a function of temperature), V_{dc} is the dc self-bias voltage and N is the number of reactive species in the plasma (a first order chemical reaction is assumed). The

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measurements by Lee et al. [2] and those done by Coburn [3] show that N is approximately proportional to V_{dc}.

The validity of the exponent 2.5 is questionable. Measurements of the electron density [4] do not show the same relation with V_{dc} as predicated by the Child-Langmuir law used to derive equation 1.

In this study two kinds of etch experiments will be performed to determine the value of the exponent experimentally for the different plasma: 1) the sputter etch rate of Au, Al_2O_3, SiO_2 and Mo in an argon plasma will be determined as a function of V_{dc} and 2) the Au sputter etch rate (Au does not react with either fluorine nor chlorine compounds) in fluorine and chlorine based plasmas will be determined as a function of V_{dc}.

Comparing the reactive ion etch behaviour of various materials as a function of V_{dc} with the above described data, should yield information on their etch mechanisms: Chemical etching only should yield an exponent 1, where as physical sputtering should yield an exponent equal to the one found for Au etching.

EXPERIMENTAL

The Ar, CHF_3/Ar and CF_4/O_2 experiments were carried out in a modified MRC 8630 sputter system. The 12 cm diameter etch station was used as powered substrate electrode. The electrode was covered with a 3 mm quartz plate. The temperature of the electrode was kept constant at 50°C. The 20 cm diameter stainless steel counter electrode was mounted 7.0 cm above the quartz plate. It was electrically connected to the grounded dark space shield of the etch station.

The glass chamber was pumped by a diffusion pump, backed by a rotary vane pump. The base pressure of the system was $<2*10^{-6}$ torr. The gas flows were controlled by electronic mass flow controllers. The operating pressure was regulated by means of a throttle valve.

RF power from a 13.56 MHz generator was applied by means of a blocking capacitor. The rf power was measured on a thru-line wattmeter in the cable between generator and matching network. The dc self-bias voltage was measured with a dc voltmeter (20 Mohm) connected through a low pass filter to the powered bottom electrode [5].

The Cl_2, BCl_3 and some of the Ar experiments were carried out in a modified Balzers BA510 diode sputter system described in a previous paper [6]. The powered substrate electrode was covered with a 3 mm quartz plate.

Etchrates were determined by measuring the etched step heights using a talystep.

To improve the thermal contact between the wafers and the cooled electrode vacuum grease was applied on the back of the wafers.

Two inch <100> n-type (2-5 Ohm cm) Si wafers were used for the experiments. 1.0 um thick SiO_2 films were deposited in a PECVD AMP 3300 reactor. 1.0 um thick Au and Al_2O_3 films were sputter deposited in a Randex 2400 (8L) diode sputter system at 300 and 400 watt respectively. In the case of Au a thin Mo layer was deposited on the bare Si to prevent a reaction of the Si with Au. The Al_2O_3 etch rate depended slightly on the deposition parameters (i.e. the etch rate decreased with increasing deposition power). For comparison, the etch rate of single crystal Al_2O_3 was 10% lower than of the sputtered Al_2O_3 used in this work. All the wafers were covered with a 0.3 um thick Mo layer, which was used as an etch mask. It was patterned using wet etching. The Mo pattern covered 50% of the wafer surface. In the case of Si etching the wafers were dip-etched in BHF to remove the native oxide, immediately prior to etching.

RESULTS

The etch rates of Al_2O_3, Al, SiO_2, Au, Si and Mo in Ar, CHF_3/Ar, CF_4/O_2, Cl_2 and BCl_3 at a power density of 1.0 watt/cm^2 are given in table I.

Table I: Etch rates (nm/min) of various materials in Ar, CHF_3/Ar, CF_4+5%O_2, Cl_2 and BCl_3 at a power density of 1.0 watt/cm^2 and a pressure of 22 mtorr.

	MRC 8630			Balzer BA510		
	Ar (58 sccm) V_{dc}=1275V	CHF_3/Ar (10/44 sccm) V_{dc}=1300V	CF_4+5%O_2 (30 sccm) V_{dc}=1150V	Ar (10 sccm) V_{dc}=820V	Cl_2 (20 sccm) V_{dc}=630V	BCl_3 (10 sccm)
Al_2O_3	4.0	36	37	4	28	42
Al	-	23	-	-	-	-
SiO_2	15.0	78	90	-	70	-
Si	-	8	55	-	244	-
Mo	12(1)	2.5(.5)	20(1)	-	109(1)	-
Au	65	51	37	80	60	-

The estimated standard deviations (1 sigma) are given in parentheses.

The dependence of the SiO_2, Al_2O_3, Au and Mo etch rates on V_{dc} at a pressure of 22 mtorr in a CHF_3(10 sccm)/Ar(44 sccm) plasma, a CF_4+5%O_2 (30 sccm) plasma and an Ar (58 sccm) plasma are shown in figures 1, 2, 3 and 4 respectively.

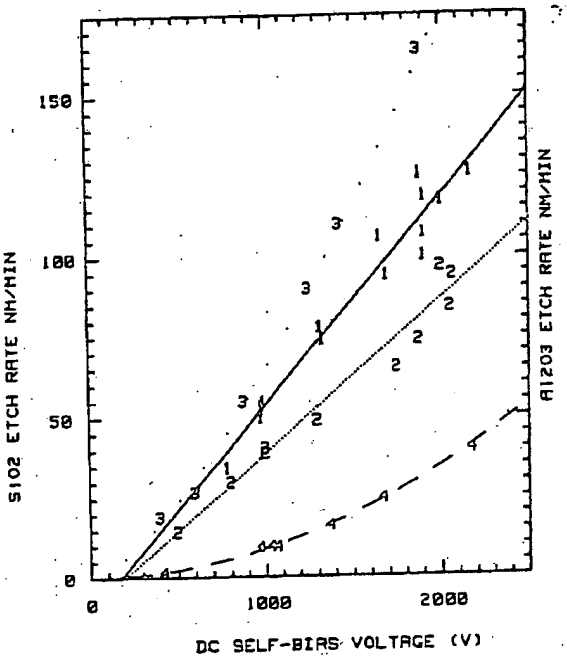

Figure 1: The SiO_2 etch rate as a function of V_{dc} at a pressure of 22 mtorr in an CHF_3(10 sccm)/Ar(44 sccm) plasma ("cold":1,-- and "hot":2,..), an CF_4+5%O_2 (30 sccm) plasma (3,. .) and an Ar (58 sccm) plasma (4,- -).

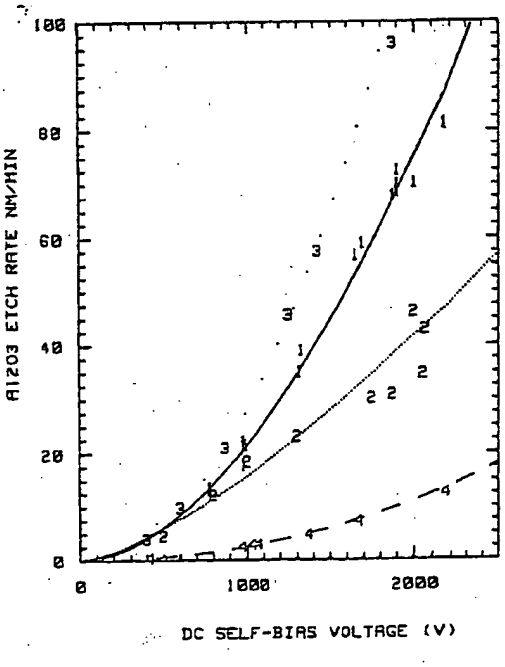

Figure 2: The Al_2O_3 etch rate as a function of V_{dc} at a pressure of 22 mtorr in an CHF_3(10 sccm)/Ar(44 sccm) plasma ("cold":1,-- and "hot"2:,..), an CF_4+5%O_2 (30 sccm) plasma (3,. .) and an Ar (58 sccm) plasma (4,- -).

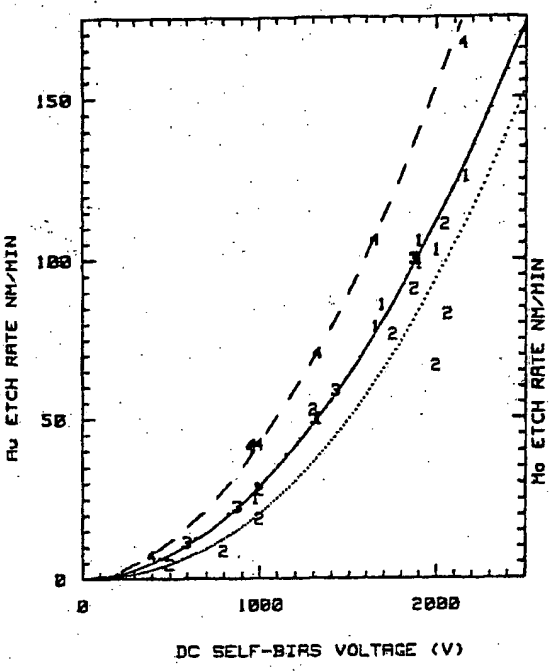

Figure 3: The Au etch rate as a function of V_{dc} at a pressure of 22 mtorr in an CHF_3(10 sccm)/Ar(44 sccm) plasma ("cold":1,-- and "hot:2,..), an CF_4+5%O_2 (30 sccm) plasma (3,. .) and an Ar (58 sccm) plasma (4,- -).

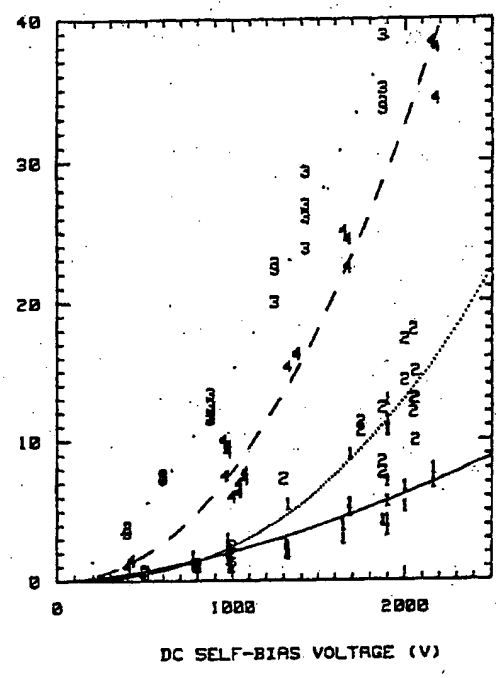

Figure 4: The Mo etch rate as a function of V_{dc} at a pressure of 22 mtorr in an CHF_3(10 sccm)/Ar(44 sccm) plasma ("cold":1,-- and "hot:2,..), an CF_4+5%O_2 (30 sccm) plasma (3,. .) and an Ar (58 sccm) plasma (4,- -).

Etch data in the CHF_3/Ar plasma are plotted for two temperature conditions, 1: the wafer made good thermal contact with the 50°C electrode by applying vacuum grease ("cold"), 2: the wafers were thermally isolated from the electrode ("hot"). It should be noted that the actual wafer temperature will probably increase with V_{dc} (power density) for the wafers that are thermally isolated from the electrode ("hot").

In table II the influence of the CHF_3 flow on the etch rates for the two temperature conditions is shown.

Table II: Etch rates (nm/min) of various materials as a function of the CHF_3 flow in a CHF_3/Ar(44 sccm) plasma at a power density of 2.5 watt/cm^2 (V_{dc}=1900V) and a pressure of 22 mtorr in the MRC8630.

	"cold" CHF_3 (sccm)			"hot" CHF_3 (sccm)		
	10	20	30	10	20	30
Al_2O_3	70(2)	70	70	32(1)	39	46
SiO_2	117(7)	119	127	76(2)	89	92
Mo	5(1)	6(1)	6(1)	12(1)	13(1)	14(1)
Au	100(2)	93(3)	89	90(1)	76	67

The estimated standard deviations (1 sigma) are given in parentheses.

Pressure variation between 8-22 mtorr in the CHF_3/Ar plasma resulted in relatively small changes in etch rate except for SiO_2 and Al_2O_3, see table III. The etch rates in the Ar plasma were independent of pressure between 10-22 mtorr.

Table III: Etch rates (nm/min) of various materials as a function of pressure in a CHF_3(10 sccm)/Ar(44 sccm) plasma at a power density of 1.8 watt/cm^2 in the MRC 8630.

	pressure in mtorr		
	8	15	22
	V_{dc}=1850 V	V_{dc}=1700 V	V_{dc}=1650 V
Al_2O_3	40	46	58(1)
SiO_2	56	72	100(6)
Mo	10(2)	8(.5)	4(1)
Au	72	75	80

The estimated standard deviations (1 sigma) are given in parentheses.

The dependence of the Si, SiO_2, Al_2O_3, Au and Mo etch rates on V_{dc} in a 22 mtorr Cl_2 (20 sccm) plasma is shown in figure 5.

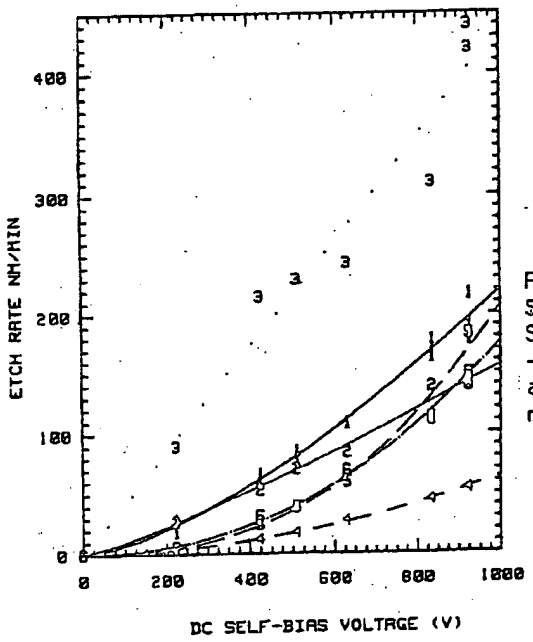

Figure 5: The etch rate of Mo on SiO_2, Al_2O_3 and Au (1,--), Mo on Si (2,..), Si (3,. .), Al_2O_3 (4,--), Au (5,-- --) and SiO_2 (6, .) as a function of V_{dc} in a 22 mtorr Cl_2 (20 sccm) plasma.

In table IV the results of least squares fits of the etch rates (shown in figures 1, 2, 3, 4 and 5) versus V_{dc} are given. The etch rates were fitted to: ER = a V_{dc}^{b}, where a and b are the constants that are calculated. The b values are given in table IV.

Table IV: Results of a least squares fit of etch rate versus V_{dc} ($ER=a\ V_{dc}^{b}$) Only the exponent b is given.

	Ar 58 sccm	MRC 8630 CHF_3/Ar 10/44 sccm	CF_4/O_2(5%) 30 sccm	BA 510 Cl_2 20 sccm
Al_2O_3	2.15(.05)	1.81(.05)	2.07(.03)	1.91(.05)
SiO_2	1.97(.05)	1.19(.06)*	1.44(.07)	2.17(.08)
Si			1.26(.10)	1.01(.10)
Mo	2.06(.08)	1.59(.15)	1.47(.03)	1.47(.05)**
Au	1.86(.04)	1.96(.06)	1.90(.03)	2.53(.14)

* a least squares fit using $ER=a+b\ V_{dc}$ gave a slightly better fit with a =-114(62) and b=0.65(.04)

** the etch rate of Mo on Si was quite different from the etch rate of Mo on Al_2O_3, SiO_2 and Au. On Si the exponent b=1.19(.05).

The estimated standard deviations (1 sigma) are given in parentheses.

DISCUSSION

The etch data for Si, SiO_2 and Au, as given in table I are in agreement with the data published in the literature, see for example van Roosmalen [7], and Lehmann and Widmer [8]. Mo shows a similar etch behaviour as Si in CHF_3/Ar and CF_4+ 5%O_2. The low etch rate in CHF_3/Ar is a result of polymer build up on the Mo surface.

The differences in sputter etch rates of Al_2O_3 and SiO_2 and of Mo and Au in the Ar plasma correspond well with the differences in the sputtering yields reported for these materials [9,10,11].

The etch rates of both Al_2O_3 and Au as a function of the power density in an argon plasma are approximately equal in both etch systems (table I). However, V_{dc} is much higher in the MRC 8630 for a given power density. The difference in V_{dc} is in agreement with the much larger dark space thickness in the MRC (2.5 cm versus 1.0 cm). In both systems V_{dc} is proportional to the square root of the power density.

The most interesting result shown in table I is the ninefold increase in the Al_2O_3 etch rate as a result of the addition of CHF_3 to the Ar plasma. This compares to a fivefold increase in the SiO_2 etch rate.

The higher Al_2O_3 etch rate in a BCl_3 plasma as compared to a Cl_2 plasma is an agreement with the literature, see e.g. [1].

Figure 1 and 2 show that the temperature behaviour of the Al_2O_3 and SiO_2 etch rates in the CHF_3/Ar plasma are similar. Both show a dramatic decrease in etch rate with increasing temperature. The Au etch rate in the CHF_3/Ar plasma (figure 3) is virtually independent of temperature and the Mo etch rate in the CHF_3/Ar plasma (figure 4) increases with temperature.

This temperature behaviour can be explained by assuming that the reactive species from the plasma desorb from the surface at higher temperature, thus slowing down the etch rate of SiO_2 and Al_2O_3. The Au etch rate should be unaffected by this effect, where as the Mo etch rate should increase because of a lower polymer formation rate.

An increase in partial pressure of the reactive species should counter act this temperature effect. This is indeed found for SiO_2 and Al_2O_3, as is shown in table II. The decrease in Au etch rate with increasing CHF_3 partial pressure could be the result of a lower sputtering yield for CF_x ions than for Ar ions and/or a decrease in electron density [4].

In an Ar plasma, i.e. under physical sputtering conditions, the etch rates of the materials studied are all roughly proportional to

V_{dc} squared, see table IV. This is significantly different from the exponent 2.5 suggested by Lee et al. [2]. The Au etch rate in the fluorine based plasmas is also roughly proportional to V_{dc} squared, confirming that the etch mechanism of Au in fluorine based plasmas is physical sputtering.

The difference in Au etch rate in the different gases is a result of different sputtering yields and different electron densities. Note that the Au etch rates in CHF_3/Ar and CF_4+5%O_2 are identical when plotted versus V_{dc} (figure 3). The etch rates in table I are given at a constant power density!

No evidence of polymer residues was found on the Au surface contrary to Mo which was covered with a thin polymer layer after etching in a CHF_3/Ar plasma. This polymer prevented the removal of the Mo in a standard wet chemical etch solution after plasma etching.

The higher exponent calculated for the Au etch rate in the Cl_2 plasma in the BA 510 could be related to the different etch system. However, this calculation was less accurate (larger sigma values) because the V_{dc} was varied over less than one decade.

The exponent 1.26 for Si in CF_4+5%O_2 corresponds well with 1.3 ± .1 calculated for Si in CF_4+20%O_2 [2] and with 1.4 ± .1 for Si in CF_4 ([13], assuming V_{dc} is equal to half of the rf peak voltage). The exponent 1.44 for SiO_2 in CF_4+5%O_2 is lower than 2.0 ± .1 calculated for SiO_2 in CF_4 [12].

A least squares fit using ER= a+b V_{dc} gave a slightly better fit for the SiO_2 etch data. This fit resulted in a X-axis intercept for SiO_2 in CHF_3/Ar of 175(95) V. This corresponds well with 141 ± 14 V calculated using van Roosmalen's data [7] and 180 ± 19 V using Chinn's data [12], fitting these data to the same equation. This X-axis intercept suggests that there is a threshold in the bombardment energy necessary for the etching to occur. The linear relation between the SiO_2 etch rate and V_{dc} indicates that chemical etching is the predominant etch mechanism.

The low values for the exponent for Si and Mo in fluorine and chlorine based plasmas indicate that chemical etching plays an important role in the etch mechanism of these materials.

The high values for the exponent for Al_2O_3 and SiO_2 in a Cl_2 plasma are in agreement with the literature [1,14]. Even though $AlCl_x$ and $SiCl_y$ are volatile, Cl_2 appears not very efficient in breaking the Si-O and Al-O bonds.

The lower etch rate of Mo on Si compared to Mo on SiO_2, Al_2O_3 and Au in a Cl_2 plasma might be the result of the high (chemical) Si etch rate. This high Si etch rate could lead to a plasma that is locally depleted of reactive species, which would result in a lower Mo etch rate. The etching of SiO_2, Al_2O_3 and Au in the Cl_2 plasma is mainly the result of ion bombardment induced etching (high exponents, see table IV), which would not lead to the depletion of reactive species.

Even though the Al_2O_3 etch rates are much higher in the fluorine based plasmas the exponents are the same as in the Ar plasma and also equal to the exponents calculated for Au. This leads to a possible etch mechanism which consists of two steps: 1) reaction of CF_z with Al_2O_3 to form AlF_x and 2) the subsequent removal of AlF_x under influence of high energy ion bombardment. The results from table IV suggest that the second step is the rate limiting step. The dramatic increase in Al_2O_3 etch rate in fluorine plasmas as compared to Ar plasmas could then be explained by assuming that the sputter yield of AlF_x is much higher than that of Al_2O_3.

Comparison of the etch profiles of Al_2O_3 and SiO_2 should yield additional information. The SiO_2 profiles always showed a 90 degree sidewall in the fluorine based plasmas, but the Al_2O_3 profiles showed a

80 degree sidewall and some trenching. Surprisingly, the sidewall angle found for the Mo mask was 90 degrees on SiO_2 and 80 degrees on Al_2O_3. However, no evidences of redeposition of Al_2O_3 or AlF_x was found on the Mo. Indeed, when a SiO_2 mask with 90 degree sidewalls was used to etch Al_2O_3 the same sidewall angle of 80 degrees was found in both Al_2O_3 and the SiO_2 mask after etching.

Linewidth measurements showed a slight decrease in linewidth with increasing etch depth. This indicates that the 80 degree sidewall is probably a result of facetting of the mask and not a redeposition phenomenon. Redeposition would result in an increase in linewidth. The Al_2O_3 profiles in an Ar plasma showed 60 degree sidewalls and redeposition of Al_2O_3 on the side of the Mo pattern was found.

Some additional SiO_2 and Al_2O_3 etch experiments were done in an Alcatel GIR 100 single wafer etcher at 1 torr, 2 watt/cm^2 in a He (80 sccm), CHF_3 (24 sccm) and C_2F_6 (24 sccm) plasma. The electrode spacing was 6 mm [15]. The SiO_2 etch rate was 0.6 um/min and the Al_2O_3 etch rate was zero. This is an extra indication that high energy ion bombardment is vital for the etching of Al_2O_3 in fluorine based plasmas.

CONCLUSIONS

In this paper it was demonstrated that Al_2O_3 can be etched in fluorine based plasmas at appreciable etch rates. An etch mechanism is proposed that consist of 1) formation of AlF_x etch products on the surface and 2) removal of these products under influence of high energy ion bombardment.

It was also shown that the measurement of etch rates as a function of V_{dc} yields valuable information in studying etch mechanisms.

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